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PRODUCTION OF HYDROCARBON-TYPE SYNTHETIC FUEL FROM WOOD (PRODUC--ETC(U)
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PRODUCTION OF A HYDROCARBON-TYPE SYNTHETIC FUEL FROM WOOD

BY

L. GARDNER

DIVISION OF MECHANICAL ENGINEERING

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Gardner, L. September 1976. 13 pp. (incl. appendices)

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(6) **PRODUCTION OF A HYDROCARBON-TYPE SYNTHETIC FUEL FROM WOOD**

(PRODUCTION D'UN COMBUSTIBLE SYNTHETIQUE DE TYPE HYDROCARBURE A PARTIR DU BOIS),

by/par

(10) **L. Gardner**

(11) Sep 76

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SUMMARY

As the world petroleum reserves become depleted considerable attention is being focussed on alternate sources of energy. In the short term, at least, the synthesis of hydrocarbon fuels similar in composition to present petroleum based fuels is the preferred choice for automotive use. Synthetic fuels of this type can be produced from coal, however the possibility of producing a similar fuel from wood has not been considered to any extent. A theoretical study of the production of fuels from wood via pyrolysis and the Fischer-Tropsch synthesis has therefore been made. The results of this study, as presented in this report, indicate that although technically feasible the production of such a fuel is financially and energy-wise uneconomical.

RESUME

A mesure que les réserves en pétrole à travers le monde s'épuisent, on s'intéresse de plus en plus à d'autres sources d'énergie. A court terme du moins, on préfère, pour l'alimentation des moteurs, réaliser la synthèse de carburants, comparables quant à leur composition aux carburants pétroliers actuels. Les carburants synthétiques de ce type peuvent être obtenus à partir du charbon; cependant, on n'a pas encore envisagé la possibilité de les produire à partir du bois. Des chercheurs ont donc entrepris une étude portant sur la production de carburants à partir du bois, par pyrolyse et synthèse de Fischer-Tropsch. Les résultats de ces études, exposés dans le présent rapport, montrent que bien qu'elle soit techniquement possible, une production de ce type ne serait rentable ni du point de vue économique, ni énergétique.

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PRODUCTION OF A HYDROCARBON-TYPE SYNTHETIC FUEL FROM WOOD

1.0 INTRODUCTION

The conversion of cellulosic materials such as plants, wood and organic waste materials to useful chemicals including fuels is currently receiving considerable attention. References 1 to 9 describe only a few of the many proposals that have been put forward for biomass conversion. In the conversion to fuels most emphasis has been towards the production of gaseous fuels such as methane and mixtures of CO, H_2 and methane for heating purposes and the production of methanol as an automotive fuel. The production of a liquid fuel of complex and indeterminate composition from waste materials and CO has been described (Refs 10 and 11). This fuel would not be considered suitable as an automotive fuel. Reference 12 suggests a combination of processes including anaerobic fermentation of pentoses and hexoses following by electrolytic decarboxylation of the caproic acid formed could be used to produce an automotive fuel. The reaction being:

$$C_6H_{12}O_6 \xrightarrow{\text{fermentation}} \underset{\text{caproic acid}}{C_5H_{11}\,COOH} \rightarrow \underset{\text{n-decane}}{C_{10}H_{22}}$$

This process appears to be highly theoretical and has not been substantiated practically. Although the use of methanol as an automotive fuel is considered by some to be the answer for a replacement for gasoline there are many technical objections to its use including the obvious one, namely its low energy content compared with gasoline. Recent work (Ref. 13) has shown that gasoline can be produced from methanol by catalytic reaction, the process however appears to be quite costly. Synthetic fuels suitable for use in automotive engines are being prepared from coal and the production of similar fuels from wood would be analogous to this situation. An attempt has therefore been made to assess theoretically the practical implications of making a liquid fuel from wood and its economics.

2.0 PYROLYSIS OF WOOD

2.1 General

The reaction products from the pyrolysis of wood consist basically of:

Wood Gas CO, CO_2, H_2, CH_4, C_2H_4 + higher molecular weight hydrocarbons.

Distillate Insoluble tar (phenolic) and pyroligneous acid, the latter containing acetic acid, methanol, acetone, esters, aldehydes and furfural.

Charcoal

The higher the pyrolysis temperature the greater the amount of gaseous products formed and at temperatures of 900-1000°C direct gasification is possible. Other factors which influence the composition of the products are rate of heating and type of wood.

The report prepared by the Pulp and Paper Research Institute of Canada (Ref. 1) contains a considerable amount of information concerning the pyrolysis of wood and the use of the resultant products to synthesize ammonia and methanol. This information is very pertinent to the production of a synthetic fuel and is used extensively in the following paragraphs.

2.2 High and Low Temperature Pyrolysis (Ref. 1)

The products from the low and high temperature pyrolysis of 1000 oven-dried tons (50% moisture content) of bark are reported to be:

	Process 1	Process 2
Pyrolysis temperature, °C	**810**	**460**
Pressure	**atmospheric**	
Products	**Composition % wt. of Feedstock**	
Wood gas	89.5	15.7
Tar	8.0	13.5
Methanol	—	3.0
Acetone	—	1.0
Acetic acid	—	1.2
Water	—	31.6
Ash	2.5	—
Charcoal	—	34.0
Wood Gas Composition	**% volume**	
CO_2	21.2	28.7
CO	27.7	27.4
CH_4	16.9	37.4
C_2H_4 and higher	8.7	—
H_2	25.5	5.0
Net heat of combustion, BTU/ft.^{3}	441	483
Total heat of combustion, BTU	13.4×10^9	2.22×10^9

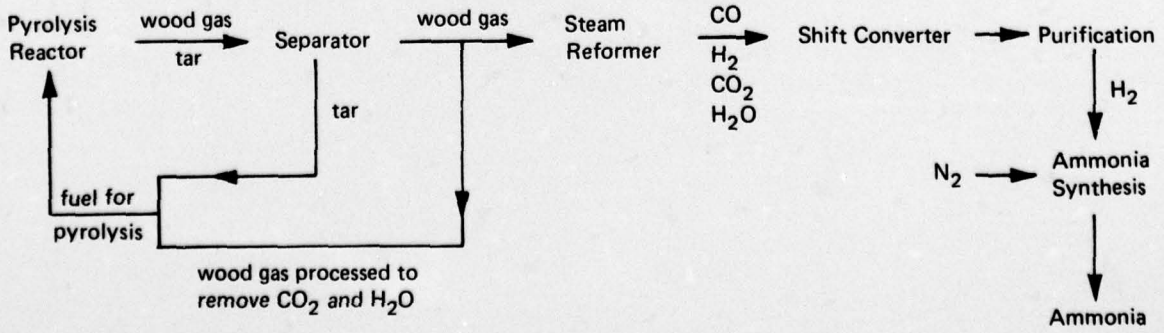
As can be seen a much larger volume of wood gas is produced by high temperature pyrolysis and although a variety of liquid chemicals are produced by low temperature pyrolysis their useful extraction would not be considered economic. The low temperature pyrolysis is not considered further.

2.3 Production of Ammonia and Methanol from Wood Gas

The use of the wood gas from the pyrolysis of 1000 ODT of bark to produce ammonia or methanol is discussed in considerable detail giving useful information relating to process conditions and economics. Since this information would be useful in assessing the possibility of producing a liquid fuel the reactions for producing ammonia and methanol will be discussed briefly.

(a) Production of Ammonia

The process for ammonia synthesis can be illustrated by the following schematic:



Approximately 73.7% of the wood gas is passed to the reformer to convert hydrocarbons to CO and H_2. The remainder of the gas plus tar is used as the pyrolysis fuel. The following reactions describe the steam reforming:

$$CH_4 + H_2O = CO + 3H_2$$

$$C_2H_4 + 2H_2O = 2CO + 4H_2$$

After reforming the gas is then passed to a converter where the water gas shift reaction is utilized to produce hydrogen

$$CO + H_2O = CO_2 + H_2$$

After purification the hydrogen is mixed with nitrogen from an air separator and catalytically reacted by the Haber process

$$N_2 + 3H_2 = 2NH_3$$

The heat of reaction from the ammonia synthesis is used to provide steam for the reformer. It is postulated that with an overall 85% efficiency 485 tons of ammonia can be produced from 1000 ODT of bark. The economics of production are not considered competitive with production from a natural gas plant of $92.90 to $85.66 per ton (not including capital investment depreciation, profit and general overheads). In 1975 market prices of ammonia range from $175 to $190 per ton.

(b) Production of Methanol

The process for methanol production is similar to that for ammonia up to and including the steam reformer where reaction to remove hydrocarbons occurs. The mixture leaving the reformer is sufficiently close to stoichiometric to avoid the need for the water gas shift reaction. The steam for the reformer in ammonia synthesis is produced by heat from the reaction between nitrogen and ammonia, this heat is not available from the methanol synthesis and therefore the wood gas has to be utilized for steam formation. This means that only 66.2% of the wood gas is available for methanol synthesis. The theoretical yield of methanol is 464 tons however the actual synthesis is only 70% efficient giving a yield of 325 tons

$$CO + 2H_2 \xrightarrow{\text{catalyst}} CH_3OH$$

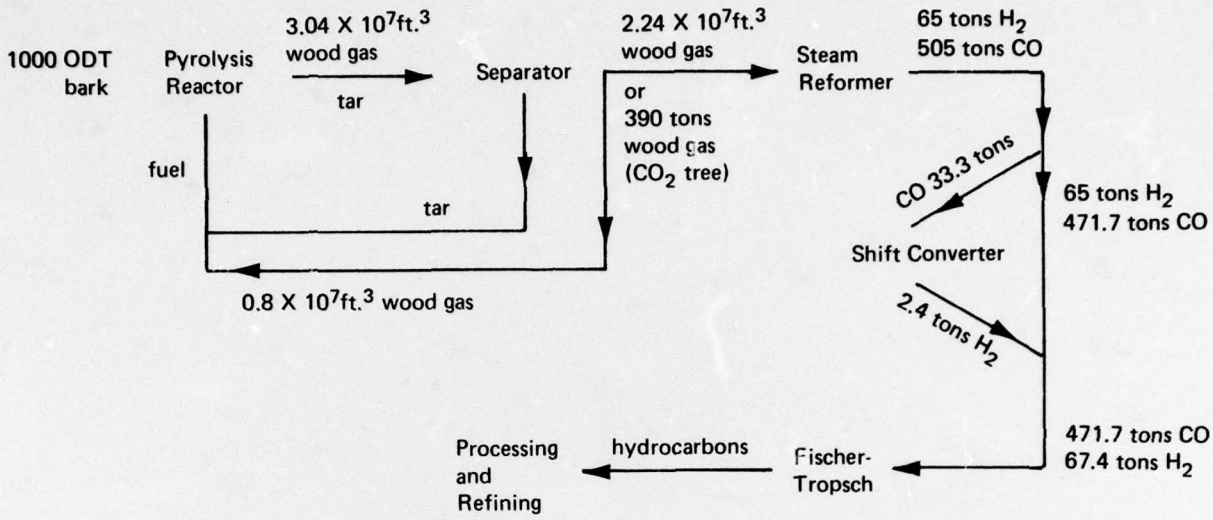
The production of methanol by this process is not considered economical. A cost per ton of $123 to $141 (± 20%) is estimated which does not include capital costs, depreciation, profit or general overheads. This can be compared with 1975 market prices ranging from $140 to $164 per ton.

3.0 PRODUCTION OF LIQUID FUEL FROM WOOD GAS

The hydrogenation of carbon monoxide to give methanol as described previously is one form of the Fischer-Tropsch synthesis, a reaction which can also be used to produce hydrocarbons. The Fischer-Tropsch synthesis received considerable attention prior to and during World War II and a resumé of this synthesis is given in Appendix A.

Applying the Fischer-Tropsch synthesis to the wood gas from the pyrolysis of 1000 ODT of bark would involve similar processing to that used for ammonia and methanol up to the point of final synthesis. The relationship to the ammonia synthesis, as far as heat generated and required, is sufficiently close to use these process details for hydrocarbon synthesis. The schematic of the process follows:

FISCHER-TROPSCH SYNTHESIS



As can be seen from the diagram approximately 74% of the wood gas is used for processing, the remainder plus tar for pyrolysis. In the steam reformer the CH_4, C_2H_4 and other hydrocarbons are converted to CO and H_2

$$CH_4 + H_2O = CO + 2H_2O$$

$$C_2H_4 + 2H_2O = 2CO + 4H_2$$

To obtain a $2:1::H_2$:CO mixture 33.3 tons of CO are reacted with steam in a shift converter to give the additional hydrogen required (2.4 tons)

$$CO + H_2O = H_2 + CO_2$$

The final mixture entering Fischer-Tropsch synthesis is 471.7 tons CO and 67.4 tons H_2.

Yields quoted in the literature vary depending upon process conditions, typically a 70-80% CO conversion is possible. The yield from the normal pressure synthesis quoted in Appendix A is approximately $150 g/m^3$ of synthesis gas (At STP). Using this value we can calculate a yield from the synthesis gas produced from the pyrolysis of 1000 ODT of bark. It will be assumed that this yield represents a "synthetic crude oil" which can be usefully processed to produce an automotive fuel.

Composition of synthesis gas = 471.7 tons CO + 67.4 tons H_2 = 539.1 tons

$$\text{Average molecular weight} = \frac{539.1}{\frac{471.7}{28.01} + \frac{67.4}{2.016}} = 10.723$$

$$\therefore \text{ At STP 539.1 tons will occupy } = \frac{539.1 \times 2000 \times 453.59 \times 22.414}{10.723} = 1.02227 \times 10^6 m^3$$

With a yield of $150 g/m^3$ total yield of synthetic crude = 169 tons or 4.5146×10^4 gallons (sg 0.75)

3.1 Energy Requirements

The amount of wood gas used for processing was approximately 74% of that produced, the same as for ammonia. To confirm whether this was a reasonable assumption the energy requirements for the synthesis and the energy produced can be calculated to see if they are in reasonable balance.

Energy required

Pyrolysis of 1000 tons	=	3.52×10^9 BTU (Ref. 1)
Steam reformer	=	1.94×10^9 BTU (Ref. 1)
Total		5.46×10^9 BTU

Energy produced

Combustion of 0.8×10^7 ft.^{3} wood gas	=	3.52×10^9 BTU (Ref. 1)
Fischer-Tropsch synthesis	=	2.44×10^9 BTU*
Total		5.96×10^9 BTU

The energy balance is reasonably good showing a surplus of 0.5×10^9 BTU which can account for losses.

3.2 Economics of Synthetic Fuel Production

Detailed information concerning the cost of bark and other wood residues is given in Reference 1. Typical cost for bark is of the order of $20.00 per ton depending upon location. The cost of the "synthetic crude" based on the price of raw material alone is therefore *44.3 cents per gallon or $15.50 per barrel.*

Table III-VII from Reference 1 (presented as Appendix B to this report) presents a detailed breakdown of the cost of producing ammonia at a hypothetical plant in Thunder Bay. *Assuming* the cost of producing "synthetic crude" is similar to ammonia, since similar processing is used we can use this data to obtain an approximate price for "synthetic crude".

Cost of producing ammonia (Appendix B) = $92.90/ton including a wood cost of $36.67/ton NH_3

Since only 169 tons of "synthetic crude" are produced compared with 485 tons of ammonia the wood cost will be $105.33/ton

Differential = $68.66

$\therefore$ Cost of producing "synthetic crude" = $161.56/ton (Not including capital investment, transportation to refinery, taxes and profits).

This is equivalent to *$0.61 per gallon* (sg 0.75) or *$21.35 per barrel* (This price can be compared to natural crude). This estimate is probably optimistic because:

(a) Transportation of wood to the pyrolysis unit would be higher because much larger quantities would be required and would have to be collected from over a wider area and

(b) The Fischer-Tropsch synthesis is more complex than the Haber type ammonia synthesis and would be more expensive.

---

* Based on a heat of reaction of 7,200 BTU/lb. of liquid product (Ref. 19).

3.3 Thermal Efficiency

Heat content of 1000 OTD bark @ 8,500 BTU/lb. $= 1.7 \times 10^{10}$ BTU

Heat content of synthetic crude produced @ 18,850 BTU/lb. $= 6.37 \times 10^{9}$ BTU

$= 37.5\%$

It is interesting to note (Ref. 19) that 3.45 tons of coal can produce 1 ton of primary product via gasification and Fischer-Tropsch synthesis. Using wood, 5.92 tons are required to produce 1 ton of primary product.

4.0 CONCLUSIONS

Although it would be technically feasible to produce a liquid hydrocarbon fuel from the pyrolysis of wood there are several drawbacks to the process:

(a) Economically the process is not competitive with the production of fuel from natural crude. Even if the price estimated in this report became competitive because of increased crude costs the capital investment requirement, which would also be increasing, would be prohibitive. In addition to the cost of the pyrolysis and processing plants a complete refinery, designed specifically to handle the wood produced "crude", would be required.

(b) Increasing transportation costs would be expected as forest areas become consumed and the wood has to be brought in from further afield.

(c) The advantage of producing fuel from coal, as typified by the SASOL operation, (See Appendix A and Ref. 17) is that the coal is concentrated in specific locations underground rather than spread across large areas of the earth surface. A very large area of wooded land would have to be used to produce the large quantities of liquid fuel required to satisfy the market demands. These quantities are much greater than the market for chemicals such as ammonia, methanol and benzene described in Reference 1.

(d) The current market for wood for conventional uses is such that little if any could be made available for fuel production. It would be doubtful if sufficient wood waste such as sawdust or bark would be available to satisfy the fuel market and in addition the market for these wastes is expanding, again leaving insufficient surplus.

(e) The thermal efficiency of the operation is very poor and it would be much more energy conserving to use the heat from the combustion of the wood itself, or the wood gas, to generate electricity.

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APPENDIX A

A.1 FISCHER-TROPSCH SYNTHESIS

A.1.1 Background

The production of liquid hydrocarbons by the catalytic hydrogenation of carbon monoxide was reported by Fischer and Tropsch in the early 1920's (Ref. 14). Prior to World War II a considerable amount of development work was conducted to improve the process. Between 1936 and 1939 nine plants were constructed in Germany with a total rated annual output of 740,000 metric tons of synthetic oil. At the same time one plant was constructed in France and one in Manchuria. All these plants produced the synthesis gas ($CO + H_2$) by gasification of coal, coke or lignite. The maximum annual output achieved in Germany was in 1943 when 585,000 metric tons of synthesis products comprising 46% gasoline, 23% diesel oil, 3% lubricating oil and 28% waxes, detergents and fats (Ref. 15). Towards the end of the war in 1943-44 most of the plants had been badly damaged by bombing and they did not resume operation. Two plants operated for a short time making refined waxes and speciality chemicals but not synthetic fuel.

Following the war a considerable amount of investigational work was conducted by the US Bureau of Mines utilizing information collected from Germany, however no successful commercial production of hydrocarbon fuels by the Fischer-Tropsch synthesis has taken place in the US (Ref. 16). The only known commercially successful plant operating the Fischer-Tropsch synthesis for synthetic fuels is SASOL in South Africa where the low price and ready availability of a low grade coal make the process economically feasible. At the present time this plant, SASOL 1, is producing a wide variety of chemicals in addition to gasoline (Ref. 17). Plans are in hand to develop SASOL 2 which will ultimately expect to use 40,000 tons of coal per day and produce 25% of the Nations gasoline (Ref. 18).

A.1.2 Process Description

The Fischer-Tropsch synthesis produces a range of hydrocarbons in addition to aliphatic alcohols, aldehydes and acids. The type and quantity of the yield depends upon:

Operating pressure

Catalyst

Operating temperature

Reactor design

A considerable amount of work was conducted in Germany and later at the US Bureau of Mines to investigate the effects of these parameters, particularly catalyst type and manufacture (Refs 15 and 16). The optimum temperature ranges are 170-205°C for nickel and cobalt catalysts, 200-325°C for iron catalysts and 160-225°C for ruthenium. Nickel catalysts are best operated at atmospheric pressure (normal pressure synthesis) iron up to 20 atmospheres (medium pressure synthesis) and ruthenium at 100 atmospheres (high pressure synthesis). The high pressure ruthenium synthesis is utilized mainly to produce high molecular weight waxes. The basic reactions involved in the Fischer-Tropsch synthesis can be summarized as follows:

$$(2n + 1)\, H_2 + nCO = C_nH_{2n+2} + nH_2O$$

$$2n\, H_2 + nCO = C_nH_{2n} + nH_2O$$

$$(n + 1)\, H_2 + 2nCO = C_nH_{2n+2} + nCO_2$$

$$nH_2 + 2nCO = C_nH_{2n} + nCO_2$$

Other equations can be written to describe the preparation of oxygenated materials. References 15 and 16 give examples of the composition of products from a typical commercial scale normal pressure and medium pressure synthesis. This data is shown below:

Constituent	Wt. %	Olefins Vol. %	C Number	Research Octane No.	Cetane No.
Normal Pressure Synthesis (CO Catalyst)					
Gasol ($C_3 + C_4$)	12	50	C_3, C_4		
Gasoline to 185°C	49	37	C_4, C_{10}	52	
Gasoline to 200°C	54	34	C_4, C_{11}	49	
Diesel Oil, 185-320°C	29	15	C_{11}, C_{18}		100
Diesel Oil, 200-320°C	24	13	C_{12}, C_{19}		105
Soft Paraffins, >450°C	7		$>C_{19}$		
Hard Paraffins, >450°C	3				
Total yield 148g per m^3 synthesis gas					
Medium Pressure Synthesis (CO Catalyst)					
Gasol ($C_3 + C_4$)		30	C_3, C_4		
Gasoline to 185°C	35	20	C_4-C_{10}	28	
Gasoline to 200°C	40	18	C_4-C_{11}	25	
Diesel Oil, 185-320°C	35	10	C_{11}-C_{18}		100
Diesel Oil, 200-320°C	35	8	C_{12}-C_{19}		105
Soft Paraffins, 330°C	30		C_{19}		
Total yield 145g of liquid products + 10g gasol per m^3 synthesis gas					

The hydrocarbons from the synthesis require further processing to provide gasoline of suitable quality and although the diesel fuel has a good cetane rating it contains some olefins. In the examples given yields of about 150g of product per m^3 of synthesis gas are obtained. Similar data, 120-135g/m^3 is given in Reference 19 which is equivalent to about 70% CO conversion.

APPENDIX B

TABLE III-VII

COST CALCULATION OF A WOOD WASTE BASED AMMONIA

Location: Thunder Bay		
Total capital investment, wood gasification Capacity 3090 tons wood/24 hrs Cost-capacity exponent: 0.72		$ 20,300,000
Total capital investment, ammonia plant Capacity 1500 tons ammonia/24 hrs Cost-capacity exponent: 0.68		$100,000,000
Raw Material		
Wood waste, $17.80/ton	$36.67/ton NH_3	
Chemicals and catalysts	0.70/ton NH_3	
Utilities		
Power, 150 kWh/ton, $0.01/kWh	1.50/ton NH_3	
Boiler feed water (make-up), 1000 gal./ton, $1/1000 gal.	1.00/ton NH_3	
Cooling water (make-up), 2500 gal./ton, $0.25/1000 gal.	0.63/ton NH_3	
Labour-dependent Operating Cost		
Labour, 8 men/shift, $5/man hour	0.64/ton NH_3	
Labour overhead, 100% of Labour	0.64/ton NH_3	
Capital-dependent Operating Cost		
Maintenance, 7% TCI/year	13.34/ton NH_3	
Operating cost gasification ($3/ton wood)	6.18/ton NH_3	
Total Production Cost		$61.30/ton NH_3
Loading		1.00/ton NH_3
Sales and Marketing, 6% of selling price		11.10/ton NH_3
Transportation		19.50/ton NH_3
Tariff		NIL
Total Product Cost		$92.90/ton NH_3